Ultrasonic in-line monitoring of styrene miniemulsion polymerization

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HIGHLIGHTS

- Ultrasound attenuation is used to monitor miniemulsion polymerization of styrene.
- In the early stage thermoelastic effect dominates the attenuation.
- From the change in thermoelastic contrast we calculated the conversion.
- In the later stage of polymerization attenuation shows a maximum.
- The maximum originates from the glass transition in the polymer particles.

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ABSTRACT

Ultrasonic transmission is a simple, non-destructive method to characterize turbid systems like e.g. emulsions or polymer dispersion. Here we use this technique for in-line monitoring of the miniemulsion polymerization of styrene. Either the ultrasound attenuation or the velocity signal provides a fingerprint characterizing the reaction process. During the reaction process the sound velocity increases by about 150 m/s and the attenuation coefficient \( \alpha \) changes by more than 75%. In the early stage of polymerization the thermoelastic effect dominates \( \alpha \) and accordingly \( \alpha \) decreases when more and more polymer chains are generated. In this regime the fractional conversion of monomer to polymer \( X \) is obtained from a calibration of the \( \alpha \) values using gravimetrically determined \( X \) data. In the later stage of the process polymer relaxation dominates and \( \alpha \) goes through a sharp maximum when the reaction temperature matches the dynamic glass transition temperature \( T_{g,\text{dyn}} \) of the polymer/monomer mixture within the droplets. Then \( X \) can be directly calculated from \( T_{g,\text{dyn}} \) without calibration only using physical material parameters for the given monomer/polymer system, and the corresponding data are in excellent agreement with gravimetrically determined values.

This method may be applied to the emulsion polymerization of other monomers, but also for monitoring solution polymerization processes as long as the reaction temperature \( T_R \) is below \( T_{g,\text{dyn}} \). In case of emulsion polymerization the initial decay of \( \alpha \) may also be used for process control for systems, which exhibit a change in thermoelastic contrast during polymerization, even if \( T_R > T_{g,\text{dyn}} \), but needs additional calibration.

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1. Introduction

Emulsion polymerization is a process of great industrial importance for manufacturing of latex paints, adhesives, coatings, paper and textile binders, and synthetic rubber. The need for constant product properties, the reduction of time-to-market, the continuous optimizing of reactor yield, and operation time, as well as the improvement of the safety and the ecological issues lead to high demand for more advanced methods to control the production process. Typical parameters of interest during polymerizations are conversion and reaction rate, molecular weight, chain length distribution, copolymer composition, as well as particle size distribution and concentration.

Calorimetric measurements have a long tradition to measure the conversion and reaction rate on-line [1]. Optical techniques such as near-infrared (NIR), mid-infrared (MIR), Raman, UV/Vis, or fluorescence spectroscopy, which can be used for simultaneous monitoring of monomer conversion, particle size, comonomer concentration during copolymerizations, are promising but are still on the research level [1,2]. Other on-line methods used on the industrial scale are based on densiometry, surface tension, or chromatographic methods involve sophisticated flow through cells, placed in-line the latex stream [2]. This is critical because the polymer emulsions are sensitive to shear and tend to form polymer films and can clog the measurement device. Another problem is that...
methods such as chromatography are time consuming. This delay time can be critical for process control. Ultrasound velocity and attenuation in liquid media can be measured easily in real time. The sensors are inexpensive and can be directly plugged in the reaction mixture. Here we have investigated ultrasound transmission to monitor miniemulsion polymerization of polystyrene (PS) in situ.

A sound wave travels in a medium by a displacement of matter. The molecules oscillate due to the interplay of viscoelastic forces and inertia. In liquids the complex wave number \( k \) depends on the angular frequency \( \omega \), the adiabatic compressibility \( \kappa \) and the density \( \rho \) [3]:

\[
\frac{k}{\omega} = (\rho \kappa)^{1/2}
\]

(1)

The complex wave number consists of a real part and an imaginary part, the latter describes the intensity loss of the wave:

\[
k = \frac{\omega}{c} + i \xi
\]

(2)

Here \( c \) is the sound velocity and \( \xi \) is the attenuation coefficient. In pure water and styrene \( \xi \) is small and can be neglected. In disperse systems \( \xi \) depends on the attenuation of the continuous phase \( x_0 \), the attenuation due to visco-inertial losses \( x_{\text{i}} \), the attenuation because of thermo-elastic losses \( x_{\text{T}} \), scattering by the dispersed particles \( x_p \), and relaxational losses \( x_{\text{g}} \). For the case of simplicity we ignore coupling between these phenomena and write the total attenuation just as the sum of all mentioned contributions (Eq. (3)). For dilute systems this seems to be a reasonable approximation.

\[
\xi = x_0 + x_{\text{i}} + x_{\text{T}} + x_p + x_{\text{g}}
\]

(3)

For polymer particles and emulsions with droplet sizes much smaller than the wavelength of the acoustic wave\(^1\) attenuation is dominated by thermo-elastic and relaxational losses. The influence of the thermo-elastic effect on the wave number can be described by the Isakovitch model. For moderate absorptions (\( \xi < k \)) the model gives the following expression for the thermo-elastic losses [4]:

\[
\xi_{\text{I}} \lambda \propto \left( \frac{\beta_1}{\rho_1 c_{\text{p}1}} - \frac{\beta_2}{\rho_2 c_{\text{p}2}} \right)^2 \times g(\omega r^2)
\]

(4)

with the wave length \( \lambda \) and the function \( g(\omega r^2) \) which depends only on the droplet radius \( r \) and the angular frequency \( \omega \), and moreover \( \rho_1, \beta_1 \) and \( c_{\text{p}1} \) are the density, the thermal expansion coefficient, and the specific heat capacity at constant pressure of medium 1. The indices 1 and 2 represent the particle and the continuous phase, respectively. At a constant frequency and constant droplet size the expression is only influenced by thermo-physical constants. Since \( \xi_{\text{I}} \) is size-dependent it can be used for droplet or particle sizing in dispersions or emulsions. This has been successfully demonstrated for emulsions of silicone oil in water [4]. But for dispersions of PS-particles in water \( \xi_{\text{I}} \) is negligibly small compared to the relaxational losses, especially in the vicinity of the glass transition. The frequency dependence of the relaxational losses in polymer particles is given by [5]:

\[
\xi_{\text{R}} \lambda \propto \frac{\alpha \tau}{1 + \omega^2 \tau^2}
\]

(5)

with the relaxation time \( \tau \). Organic compounds of low molecular weight such as monomers and plasticizers reduce the energy barrier for molecular rearrangements of the polymers and lead to decreasing relaxation times. To measure the spectra of the relaxational losses either the frequency or the relaxation time has to be varied. The relaxation time can be changed by variation of temperature. For aqueous dispersions of polyvinyl acetate (PVAc) [6,7] and of polyvinyl acrylat-copolymer particles [8] it has been demonstrated, that relaxation losses strongly dominate the total attenuation at temperatures between 20 °C and 65 °C. The temperature at which the attenuation \( x_{\text{g}} \) goes through a maximum is defined as the dynamic glass transition temperature \( T_{g,\text{dyn}} \) [6–8], which is quantitatively related to the glass transition temperature \( T_g \) as determined e.g. by calorimetric or dynamic-mechanical analysis according to the time–temperature superposition principle [9].

Research on ultrasonic techniques for process control purposes during emulsion polymerization dates back to the 1980s. Hauptmann et al. [7,10] investigated the emulsion polymerizations of vinyl acetate (VAC) by ultrasound. More recently Morbidelli et al. used ultrasound velocity measurements to monitor monomer conversion \( X \) during the emulsion copolymerization of methyl methacrylate (MMA) and VAC [11,12]. In these publications the conversion was calculated from the ultrasound velocity by using empirical models and calibration.

In this work we apply ultrasound to monitor the miniemulsion polymerization of styrene [13,14]. Miniemulsions are stable and consist of very small droplets (0.01–0.5 μm). Because of the stability of miniemulsions it was possible to study the acoustic properties during the reaction without stirring in a custom made analytical ultrasonic measuring cell. The ultrasonic signal is dominated by the thermoelastic effect in the initial stage of polymerization, since the thermoeelastic contrast between water and styrene is different from that between water and polystyrene, and the decrease in \( \xi \) is related to the polymerization rate. After calibration this effect can be used to measure the fractional conversion of monomer \( X \) at the beginning of the reaction. Polymeric relaxation processes determine ultrasound attenuation in the later stage, when \( T_{g,\text{dyn}} \) is close to the reaction temperature. Then \( X \) can be calculated from \( T_{g,\text{dyn}} \) for the time where \( x \) goes through a maximum without further calibration or model assumptions.

2. Materials and methods

2.1. Materials

Stabilized styrene, sodium dodecyl sulfate (SDS), potassium peroxodisulfate (KPS), 1-hexadecanol (HD), and hydroquinone were supplied by Sigma–Aldrich. Ethyl benzene and NaHCO₃ was purchased from Carl-Roth (Karlsruhe, Germany). Double-distilled water (ddH₂O) was used in all experiments. All chemicals were used without any further purification.

2.2. Miniemulsion polymerization

The miniemulsion was prepared according to a standard recipe [15] (Table 1). HD was dissolved in styrene by using a magnetic stirrer. After addition of SDS and the initiator KPS with NaHCO₃ the solution was filled up with double-distilled water to get the desired total mass. The mixture was cooled in an ice bath and emulsified by ultrasonification with a 1/2” horn and 50% amplitude for 5 min (Branson Sonifier S-250D). The mixture was heated within 30 min from 20 °C to the final reaction temperature.

2.3. Ultrasound measurement

For ultrasonic measurements we used a custom made thermostated transmission cell with a sample volume of 15 ml (Fig. 1). The piezo-transducers provided by the German Institute for Polymers (Deutsches Kunststoff-Institut, DKI) had a diameter of 2 cm and the distance between transmitter and receiver was \( d = 1 \) cm. They were operated in the pulsed mode at a frequency of 3 MHz as spec-

\(^1\) Diameter \( \ll \) \( \lambda \) or frequency \( \approx 1500 \text{ m/s} \times 3,000,000 \text{ s}^{-1} = 500 \mu \text{m}. \)
Table 1
Recipe for the miniemulsion polymerization of styrene for a sample volume of 20 ml.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Volume or weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>ddH₂O</td>
<td>80 parts</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>10 mM</td>
<td>320 µl 0.5 M SDS/46.1 mg</td>
</tr>
<tr>
<td>HD</td>
<td>30 mM*</td>
<td>116.4 mg</td>
</tr>
<tr>
<td>KPS</td>
<td>0.5, 0.7, 1, 3, 5, 7, 10 mM*</td>
<td>80, 112, 160, 480, 320, 1120, 1600 µl of 0.1 M KPS/NaHCO₃-solution</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Same as KPS*</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>20.2 parts based on the water</td>
<td>4.00 g</td>
</tr>
</tbody>
</table>

* In the aqueous phase.

Fig. 1. Scheme of the ultrasonic measuring cell.

ified by the manufacturer. We used a PC equipped with an SR-9000 pulser card and a SR-9010 receiver card from MATEC Instruments (Northborough, USA) for pulse generation and response measurement of the piezo-transducers. The sound velocity c was determined from the measured running time t(T) of the first signal after each pulse, the delay time of the device t₀(T), and cell width d:

\[ c(T) = \frac{d}{t(T) - t₀(T)} \]  

(6)

The delay time of the device was calculated from the time shift in water t_water(T) and the theoretical sound velocity of water c_water(T) [16] as follows:

\[ t₀(T) = t_water(T) - \frac{d}{c_water(T)} \]  

(7)

For determination of the attenuation coefficient α we measured the maximum voltage U(T) of the first signal generated by the piezo receiver, and the corresponding amplitude in degassed water U₀(T) [8]:

\[ α = \frac{1}{d} \ln \left( \frac{U₀(T)}{U(T)} \right) \]  

(8)

The data for t₀(T) and U₀(T) for the respective temperature was obtained from a second order polynomial fit to the data of the calibration with degassed water. The temperature was controlled to an accuracy of ±0.01 °C using a computer controlled thermostat filled with silicone oil. Samples could be taken directly out of the cell by a syringe through a septum. Replacement of the septum with a pressure cap and application of a pressure of 5 bar allowed to analyze aqueous dispersions at temperatures between 0 °C and 130 °C. The temperature dependency of the ultrasonic attenuation was measured at a heating rate of 2 K/min.

3. Results and discussion

3.1. Ultrasonic attenuation of swollen polystyrene particles

In the first step the influence of monomer on the ultrasound attenuation of industrial polystyrene dispersions was evaluated. This has been done by variation of the temperature. To avoid reactions of the added styrene at high temperatures ethyl benzene was used instead. In Fig. 2a the change of attenuation coefficient α of polystyrene latexes swollen with ethyl benzene is plotted against temperature T. Similar experiments have been done using styrene as swelling agent. Here ϕ₁ denotes the volume fraction of ethyl benzene with respect to the dispersed phase. A maximum of the attenuation coefficient could be observed in the accessible temperature range for mixtures with ϕ₁ between 9% and 41%. The temperature at the peak is denoted as the dynamic glass transition temperature T_g,dyn. Far away from T_g,dyn the attenuation is close to the experimental error of ±5 m⁻¹. At T_g,dyn the values for the attenuation coefficient are in the range between 70 and 100 m⁻¹. This allows to measure T_g,dyn with an accuracy of less than ±2 °C for both swelling agents. Fig. 2b illustrates that T_g,dyn ≈ 45 °C agrees well with the glass transition temperature T_g of solutions of polystyrene in ethyl benzene measured by differential scanning calorimetry (DSC) [17]. The relationship T_g,dyn ≈ T_g + 45 °C for polystyrene is a consequence of the high frequency at which polymer relaxation is probed in ultrasonic experiments and can be calculated from the WLF-equation [18]. The theoretical values were calculated according to the approach of Pochan et al. [19]:

\[ \ln T_g = \phi_1 \ln T_{g1} + \phi_2 \ln T_{g2} \]  

(9)

with the glass transition T_gi, and the volume fraction ϕ_i of compound i. The volume fraction ϕ₁ + ϕ₂ = 1 relates to the polymer 1.

2.4. Samples

Industrial polystyrene latexes (Dow Chemicals) with a particle size of 380 nm were used to study the ultrasound properties of swollen latex particles. Mixtures of polymer dispersion and the organic solvent ethylbenzene were stirred for at least 10 min before the ultrasonic measurement. During this time the organic solvent was completely absorbed by the particles as confirmed by transient ultrasound attenuation measurements at constant temperature. The temperature dependence of α and ν was determined for mixtures with polymer/solvent ratios between 0.1 and 0.7.

To analyze the temperature dependency of the ultrasonic signals during the polymerization process after different reaction times, the reaction was conducted in a 400 ml round bottom flask equipped with a condenser. 200 ml of the mixture with 5 mM KPS was filled in the flask and stirred for 2 h at 70 °C. Samples were taken every 20 min. The reaction was stopped by addition of 0.5 w% hydroquinone with respect to the organic phase. The temperature dependency of α and ν of each sample was analyzed. X was determined gravimetrically using a Halogen Moisture Analyzer HR83 (Mettler Toledo, Switzerland). The accuracy of the gravimetric measurement is around 1% because of residual monomer and inhomogeneities, such as aggregated latex particles and/or monomer droplets.

For the online ultrasonic measurements during the polymerization reaction 20 ml of the miniemulsion were prepared. Around 15 ml of the mixture were filled and polymerized in the ultrasonic measuring cell. For calibration and in order to benchmark the values determined in-line, samples of 1 ml were taken after 60 and 90 min polymerization time by a syringe through the septum. X was determined gravimetrically after addition of hydroquinone the same way as described above.
and the organic solvent 2 which are dispersed in the aqueous phase. The glass transition temperature for supercooled ethyl benzene of $-158^\circ$C used in the calculation was determined by Yamamura et al. [20]. The data shown in Fig. 2b confirms that $T_g,\text{dyn}$ of polystyrene dispersions swollen by styrene is close to that of the polystyrene/ethyl benzene mixtures. Obviously, the added organic solvent is completely absorbed by the polymer particles without any further polymerization.

3.2. Ultrasonic attenuation of miniemulsions after different reaction times

During the emulsion polymerization process the composition and the physical properties of the dispersed phase are changing. At the beginning the mixture is a homogeneous emulsion of monomer and co-stabilizer in water. Upon heating the mixture the initiator KPS dissociates and forms radicals which enter the monomer droplets. The polymers are formed by the successive addition of the styrene monomers to the initiated free radical. While the chain length increases the movement of the bulky macromolecules is getting more and more restricted, and eventually entanglements between the polymer chains occur. The glass transition temperature increases during the polymerization process since the amount of polymer within the droplets increases at the expenses of monomer.

We wanted to demonstrate, that polymeric relaxation within the mixed monomer/polymer-droplets changes the ultrasonic attenuation in the later stage of the reaction process. Therefore, we prepared 200 ml of emulsion and started the polymerization process as described above. In Fig. 3 the ultrasonic attenuation of the samples taken before starting the reaction and after 60, 80, and 100 min are plotted versus temperature.

The attenuation of the sample taken before starting the reaction at $t = 0$ min decreases slightly with temperature. Similar behavior was observed after a reaction time of 60 min. But the absolute value of the attenuation at this time is 50% lower than at $t = 0$ min. The observations reflect the decrease of the attenuation at the beginning of the polymerization reaction (Fig. 4a). In this case the ultrasound attenuation is dominated by the thermoelastic effect. The acoustic contrast between the particles and the surrounding fluid due to the thermo-elastic effect is given by the squared expression in brackets in Eq. (4). From the thermal expansion, the density and the heat capacity at constant pressure the thermo-elastic coefficient can be calculated. At a constant particle or droplet radius and a constant sound frequency the thermo-elastic effect is only influenced by the thermo-elastic coefficients. The values in Table 2 show that the thermo-elastic contrast between styrene and water is 2.5 times as high as between polystyrene and water, using these data one can estimate the change in $x$ within the first 60 min after starting the reaction. According to the monomer conversion at this time we estimate a drop of $x$ by a factor of 1.5, assuming linear superposition of the attenuation from the monomer and the polymer. This is in fair agreement with the change observed experimentally. After a reaction time of 80 min a maximum in $x$ can be measured at $T_g,\text{dyn} = 18^\circ$C. At this stage the relaxation processes in the polymer particles are starting to contribute significantly to the total attenuation. From $T_g,\text{dyn}$ the monomer conversion $X = 1 - \phi_s$ can be calculated according to Eq. (9). The error in $X$ is determined by the precision in the $T_g,\text{dyn}$ measurement resulting in a relative deviation in $X$ of less than 1%. The conversion of 65% determined from ultrasound attenuation agrees fairly well with the conversion of 63% measured gravimetrically. The maximum in the attenuation at $t = 100$ min is shifted to 104 $^\circ$C. At this point the absolute values of $x$ vary much stronger with temperature than for the sample taken after 80 min. At this
stage of the reaction the attenuation is clearly dominated by the relaxation process in the particles. \( T_{g,\text{dyn}} = 104 \, ^\circ\text{C} \) corresponds to a conversion \( X = 90\% \) which confirms the good agreement with the gravimetric value of 92%.

### 3.3. Ultrasound monitoring of the miniemulsion polymerization

In this part we present the results referring to the in-line monitoring of the miniemulsion polymerization. According to the results in Section 3.1 we expect a maximum in the ultrasound attenuation at the time when the dynamic glass transition temperature of the polymer particles \( T_{g,\text{dyn}} \) equals the reaction temperature \( T_R \). We analyzed the acoustic properties of the mixtures during the reaction at different rates. The overall rate of polymerization \( R_p \) of emulsion polymerizations is given by:

\[
R_p = \frac{k_p N_p [M]_p \bar{n}}{N_A}
\]

with the rate of polymerization \( k_p \), the total number of particles \( N_p \), the monomer concentration in the particles \( [M]_p \), the average number of radicals per particle \( \bar{n} \), and Avogadro’s number \( N_A \). The number of radicals per particles can be controlled by the initiator concentration. The effect of temperature on the rate of polymerization can be described by an Arrhenius equation:

\[
k_p \propto e^{-\frac{E_a}{RT}}
\]

where \( E_a \) is the activation energy, \( T \) is the absolute temperature in Kelvin, and \( R \) is the gas constant. Here we have varied the initiator concentration and temperature in order to change the reaction rate and we discuss the corresponding changes in the ultrasound signal during the polymerization.

Fig. 4 shows the ultrasound attenuation and the velocity of sound during the reaction versus time for different initiator concentrations at the similar reaction temperature. After filling the reaction mixture into the ultrasound measuring cell all emulsions show approximately the same attenuation and sound velocity. In all cases the attenuation has its highest value at the beginning of the measurement. This is due to the high thermoelastic contrast between styrene monomers within the droplets and the surrounding water. Minor variations in the initial attenuation between different samples may be due to variations in the droplet size, since the thermoelastic effect is strongly size dependent (Eq. (4)). While heating the mixture in the cell the attenuation decreases slightly. After 40 min the final temperature was reached. Without initiator the attenuation of the system decreases monotonically from 1.2 to 70 m/s. The maximum in the attenuation is reflected in the inflection point of the sound velocity. Similar results were obtained for the ultrasound velocity during the macroemulsion polymerization of MMA, VAC and MMA/VAC copolymers in a stirred batch reactor [11,12]. Eq. (2) shows that velocity and attenuation are both parts of the complex wave number. In principle \( c \) is related to \( \alpha \) by the Kramers–Kronig relation [25]. But since the bandwidth of the transducer is too small to cover a reasonable frequency range this
is not feasible here. Because a maximum of a monitored signal is easier to determine than an inflection point we focus on the discussion of the ultrasonic attenuation in the subsequent part of this paper.

The strong decrease of the thermoe-elastic contrast when styrene is progressively replaced by polystyrene (see Table 2) is a fingerprint of the reaction process and the reaction rate can be obtained from the slope of the ultrasonic attenuation (Fig. 4a). The time at which the polymerization reaction reaches its maximum (open symbols) because with increasing conversion polymer relaxation processes dominate the ultrasonic attenuation (Fig. 4a). The time at which x reaches its maximum x_{max} corresponds to the time when the reaction temperature $T_R$ equals the dynamic glass transition temperature $T_{g,dyn}$. Here $T_R = 71 \pm 1 °C$ and $T_{g, dyn} = 71 °C$ corresponds to a conversion of $X = 1 - \phi_0 = 0.81 \pm 0.01$. As expected, the time to reach this conversion decreases with increasing initiator concentration. In Fig. 6 we plot the conversion determined from the decay of x at the beginning and from the attenuation maximum $a_{max}$ in comparison to the conversion determined gravimetrically.

Within experimental accuracy the differently obtained X values agree well. Obviously, conversion is faster at higher KPS concentrations as expected. At the lower initiator concentration X increases linearly with time up to $X = 80%$. But at the highest KPS concentration of 7 mM and 10 mM the rate slows down, when about 60% conversion are exceeded.

This behavior can be qualitatively explained by the mechanism for emulsion polymerization [14]. At the beginning the rate is

\[ a_{corr} = \frac{a}{a(t = 40 \text{ min})} - \frac{a_{0 \text{ mM KPS}}}{a_{0 \text{ mM KPS}(t = 40 \text{ min})}} \]
limited by the number of radicals within the monomer droplets. The reaction rate increases with increasing radical concentration. This increase can be seen in the inset of Fig. 6 for low KPS concentrations. After the dissociation of all initiator molecules the number of radicals in the droplets and hence the reaction rate tends to be constant corresponding to the linear increase in X with increasing time as in Fig. 6. At high conversions the reaction becomes diffusion limited. First the probability for recombination of two radicals at the chain ends decreases because of the limited mobility of the entangled polymer chains. The expected increase in the overall reaction rate due to the so-called gel effect cannot be observed in the experimental results in Fig. 6 likely because of the poor time-resolution of the measured data. The experimental data clearly show the decrease of the reaction rate at KPS concentrations above 7 mM and X > 60%. This is presumably due to a slowing down of monomer diffusion as the glass transition temperature of the polymer/monomer mixture within the droplets approaches the reaction temperature. Note that the reaction goes on after reaching the dynamic glass transition T_g,dyn by because of the difference in the time scales probed by ultrasonic measurements and that of the diffusion processes for which T_g = T_g,dyn − 45 °C is relevant. The general trend of the data presented in Fig. 6 is qualitatively consistent with the literature data for the same reaction [26]. More data points are needed to give a complete picture of the polymerization process including the increase due to the gel effect. However the results show that the conversion can be determined conveniently from the decrease of x at the beginning because of the thermo-elastic contrast and the maximum in \( \alpha(t) \) at which the reaction temperature equals T_g,dyn.

To confirm our model we measured x and v during the mini-emulsion polymerization at three different temperatures and a constant KPS concentration of 5 mM. The overall rate of the reaction increases with increasing temperature according to Arrhenius (Eq. (11)). Thus increasing the reaction temperature changes the overall reaction rate in a similar way as an increase in the initiator concentration as can be seen from Fig. 7a displaying x(t) data obtained at different reaction temperatures. Again we set T_R = T_g,dyn for the time when x reaches its maximum and we calculate the conversion corresponding to T_g,dyn. Here we have to keep in mind, that the conversion rate at T(\( \tau_{\text{max}} \)) varies with reaction temperature. The good agreement between ultrasonic and gravimetric results at different temperatures confirms again that ultrasonic attenuation measurements are a convenient method for the online determination of the conversion.

**4. Conclusion**

The miniemulsion polymerization of styrene has been monitored in-line using ultrasound transmission measurements. Either the ultrasound attention or the velocity provides a fingerprint characterizing the reaction kinetics. In the early stage of polymerization the thermoelastic effect dominates and accordingly the attenuation decreases when more and more polymer chains are generated. Since the thermoelastic contrast for the droplets including a solution of polystyrene in styrene cannot be calculated using simple linear mixing rules, we use independent gravimetrically determined conversion data to calibrate the attenuation data and to calculate the conversion data corresponding to the decrease in x. In the later stage of polymerization polymer relaxation processes dominate and x goes through a sharp maximum. This is the case when the reaction or measurement temperature equals the dynamic glass transition T_g,dyn. This quantity is directly related to the conversion X and the data determined from these in-line measurements are in excellent agreement with gravimetrically determined off-line conversion data. The conversion data obtained from the initial decay of x are consistent with those obtained from the x maximum corresponding to the dynamic glass transition. The observed increase in conversion rate with increasing temperature and initiator concentration is expected for emulsion polymerization processes. If T_g of the polymer and the monomer as well as the difference T_g,dyn − T_g are known, the conversion rate X can be calculated at the time \( t(\tau_{\text{max}}) \) at which a goes through its maximum without further calibration. The method can be applied to the emulsion polymerization of other monomers like e.g. styrene, MMA, VC or VA as long as the reaction temperature is below T_g,dyn of the corresponding polymer. After calibration the decay of x at the beginning of the reaction due to the change in thermoelastic properties can also be used for process control of polymerization processes if T_R is higher than T_g,dyn.

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**References**